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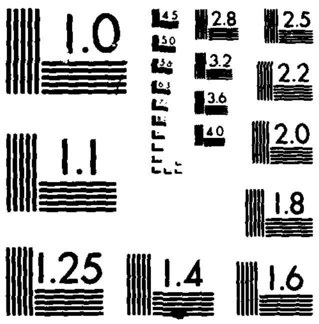
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ELECTROCHEMICAL STUDIES OF BENZOPHENONE AND FLUORENONE IMINES, AMINES AND DIPHENYLDIAZOMETHANE

by

JAMES H. BARNES, Jr.

B.S., VIRGINIA MILITARY INSTITUTE, 1972

M.A., BALL STATE UNIVERSITY,1978

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE UNIVERSITY

Manhattan, Kansas

1982

ABSTRACT

The redox behavior of several nitrogen containing derivatives of fluorenone and benzophenone has been studied. In this continuation of the study of possible precursors to carbene anion radicals, diphenyldiazomethane (Ph_2CN_2) has been studied in acetonitrile (AN) containing Me_4NPF_6 (saturated) as the supporting electrolyte. This was done to confirm that the lifetime of the anion radical ($Ph_2CN_2^{\cdot -}$) is less than 1 ms in this electrolyte system. Parker and Bethell have recently reported that electroreduction of Ph_2CN_2 in AN-Me_4NPF_6 (saturated) at a hanging mercury drop electrode is electrochemically reversible at T = 8°C and $\underline{v}$ = 100 V/s. We have shown that their interpretation is in error, and that it is an artifact of unrecognized adsorption effects on the mercury electrode. The results reported here are consistent with previous findings using platinum as the cathode, i.e., the $Ph_2CN_2^{\cdot -}$ initially formed undergoes rapid loss of molecular nitrogen ($t^{1/2} \leq$ 1 ms) to yield the carbene anion radical.

Other compounds reported are fluorenone imine (Fl=NH), N-phenylfluorenone imine (Fl=NPh), benzophenone imine (Ph_2C=NH), 9-aminofluorene ($FlHNH_2$) and 9-N,N-dimethylaminofluorene ($FlHNMe_2$). The imines have been shown to be reduced in two successive one-electron steps in aprotic mec [illegible] st to the anion radical which is stable on the cyclic voltammetric time scale and then to the unstable dianion. However, on the coulometric time scale the anion radical was also shown to undergo a series of reactions leading to the amine in high yield. Oxidation of $FlNHPh^-$ to Fl=NPh in the presence of potassium-$\underline{t}$-butoxide involves a kinetically controlled anodic peak ($\underline{E}_{p,a}$ = -0.67 V) which arises from the catalytic oxidation of $FlNHPh^-$ by

electrogenerated Fl=NPh and a second, irreversible, anodic peak at more positive potential ($\underline{E}_{p,a}$ = -0.18 V) which is attributed to the direct electrochemical oxidation of $FlNHPh^-$. Although electrocatalysis by Fl=NH is not observed in the corresponding $FlNH_2^-$ system, the ease of $FlNH_2^-$ oxidation is facilitated by the presence of K-$\underline{t}$-OBu if reduction of Fl=NH to $FlNH^{2-}$ is also made to occur. The reductions of $FlHNH_2$ and $FlHNMe_2$ result in anion radicals which have half-lives in excess of one second at $-51^{\circ}C$ and which react by unimolecular carbon-nitrogen bond cleavage. The amide anion formed by the decomposition process rapidly abstracts the C_9 proton from unreacted starting material; the other fragment anion, FlH^-, also abstacts the C_9 proton from $FlHNR_2$, but at a rate which can be followed by cyclic voltammetry. The oxidation of $FlNMe_2^-$ to the corresponding cation occurs in successive, one-electron steps in the absence of FlH^-. If reaction of the electrogenerated FlH^- with $FlHNMe_2$ is incomplete when oxidation of $FlNMe_2^-$ is effected, the intermediate radical, $FlNMe_2^{\cdot}$, is interdicted by electrocatalytically formed $FlH^{\cdot}$, presumably by coupling of $FlH^{\cdot}$ and $FlNMe_2^{\cdot}$ to give the 9-N,N-dimethylamino-9,9′-bifluorenyl, $FlHFlNMe_2$.

ELECTROCHEMICAL STUDIES OF BENZOPHENONE AND FLUORENONE IMINES, AMINES AND DIPHENYLDIAZOMETHANE

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Department of Chemistry

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Manhattan, Kansas

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I. INTRODUCTION

Beginning in 1976, our laboratory, in conjunction with the research group of Professor Richard N. McDonald, began an extensive study of a class of reactive intermediates termed "hypovalent radicals."[1] The stepwise loss of R groups from a tetravalent carbon substrate yields nine molecular fragments of neutral or unit. Four of these intermediates have received extensive study: carbanions (R_3C^-), carbonium ions (R_3C^+), free radicals ($R_3C^\cdot$), and carbenes ($R_2C\colon$). In contrast, very few studies of the other five possible intermediates(termed hypovalent radicals) have been undertaken.

One of these five, the carbene anion radical ($R_2C^{\dot{-}}$), appeared the most promising source of new information for several reasons. First, this species could conceivably act as a base , a free radical, a nucleophile, or an electron transfer agent. Secondly, since all bonding and nonbonding molecular orbitals are occupied, the possibility of skeletal rearrangements should be minimized, if not eliminated. And finally, since both gas phase and solution studies were planned, reports of the generation of carbene anion radicals in the gas phase[2] and by electrochemical reduction in solution[3,4] were promising evidence of the feasibility of studying this intermediate.

The diphenylmethylene anion radical ($Ph_2C^{\dot{-}}$) and the fluorenylidene anion radical ($Fl^{\dot{-}}$) were chosen for the initial studies since it was felt that the electronic configuration at the divalent carbon center would be different for these two species. Experimental results[2] and molecular orbital calculations[2,5] describe the electronic configuration of the ground state of simple carbene anion radicals, $H_2C^{\overline{\cdot}}$, $F_2C^{\overline{\cdot}}$, and $(CH_3)_2C^{\overline{\cdot}}$, as σ-anions and π-radical ($\sigma^2\pi^1$). It was felt that $Ph_2C^{\overline{\cdot}}$ should also have this ground state configuration with the phenyl rings twisted about their C_1-C bonds in order to relieve nonbonded repulsions. Both experiment[6] and calculations[7] showed that the ground state electronic configuration of cyclopentadienylidene anion radical ($\underline{c}$-$C_5H_4^{\overline{\cdot}}$) is $\sigma^1\pi^2$. Since $Fl^{\overline{\cdot}}$ is structurally similar to $\underline{c}$-$C_5H_4^{\overline{\cdot}}$, the ground state electronic configuration at C_9 should also be $\sigma^1\pi^2$.

Substrate structures where $R_2C^{\overline{\cdot}}$ could result from a single one-electron step were deemed desirable. Possible precursors to $R_2C^{\overline{\cdot}}$ that require three successive one-electron reductions (i.e. gem-dihalo alkanes) were ruled out because they give intermediates that potentially would react before giving rise to $R_2C^{\overline{\cdot}}$. Generally, substrates that can be photolyzed or thermalyzed to give carbenes were felt to be potential precursors to $R_2C^{\overline{\cdot}}$ upon reduction (eq. I-1 and I-2).

$$R_2CN_2 \xrightarrow{h\nu,\,\Delta} R_2C\!: + N_2 \qquad \text{(I-1)}$$

$$R_2CN_2 \xrightarrow{+e^-} R_2C^{\overline{\cdot}} + N_2 \qquad \text{(I-2)}$$

To facilitate the fragmentation, the non-carbene anion radical fragment should be thermodynamically stable, such as N_2. Thus, diazoalkanes were a logical choice for potential $R_2C^{\overline{\cdot}}$ precursors.

Initial research on "hypovalent radicals" began in our laboratory with the electrochemical reduction of diazodiphenylmethane (Ph_2CN_2) and 9-diazofluorene (FlN_2) at a platinum cathode in dimethylformamide (DMF) with 0.1 $\underline{F}$ ($\underline{n}$-Bu)$_4N^+ClO_4^-$ (TBAP) as the supporting electrolyte.[8,9] McDonald and coworkers have since reported on the chemical reductions of these species,[10] the chemical generation of $Ph_2C^{\overline{\cdot}}$ and $Fl^{\overline{\cdot}}$ from certain epoxides,[11] and the generation and ion-molecule reactions of anion radicals in a flowing afterglow apparatus.[6,12]

Our electrochemical studies of Ph_2CN_2 concluded that (1) the anion radical ($Ph_2CN_2^{\overline{\cdot}}$) once formed is very short-lived, but its lifetime (at 0^oC) is sufficient to be partially trapped by proton donors to give $Ph_2C{=}NNH_2$, (2) protonation of $Ph_2CN_2^{\overline{\cdot}}$ occurs only on terminal nitrogen, thereby precluding "ambident" behavior of this species in this and other reactions, (3) the carbene anion radical, $Ph_2C^{\overline{\cdot}}$, is formed by loss of nitrogen from $Ph_2CN_2^{\overline{\cdot}}$ and is the principal, if not the only, precursor to Ph_2CH^-, (4) the coupling of Ph_2CH^- with unreacted Ph_2CN_2 cannot involve initial electron transfer followed by coupling of $Ph_2CH^{\cdot}$ with Ph_2CN_2, (5) Ph_2CH^- is the principal chain-carrying species in the formation of benzophenone azine (the major reduction product), and (6) $Ph_2C{=}NNH^-$ also initiates azine formation, but the extent of reaction by the chain process is minor compared to that of Ph_2CH^-.[8c]

Recently, these conclusions have been questioned by other researchers.[13] They have proposed that in the absence of hydrogen atom and proton donors, $Ph_2CN_2^{\overline{\cdot}}$ is remarkably long-lived in solution, and that this anion radical displays low reactivity even toward added proton donors, e.g., diethyl malonate (DEM). These results will be contrasted in chapter III with our most recent studies of Ph_2CN_2 reduced at a hanging mercury drop electrode in acetonitrile (AN) with Me_4NPF_6 (saturated) as the supporting electrolyte.[14]

Our electrochemical studies of the reduction of FlN_2 showed a complex mechanism involving numerous electroactive intermediates and products. Results of FlN_2 reductions in the presence and absence of proton donors in DMF, AN, and butyronitrile (BN) with various supporting electrolytes at room and reduced temperatures indicate that (1) although $FlN_2^{\cdot-}$ is very short-lived, it does not lose N_2 to give $Fl^{\cdot-}$, (2) $FlN_2^{\cdot-}$ undergoes a series of reactions to give a dimeric dianion, (3) the dimeric dianion loses N_2 upon oxidation but cleaves to give $Fl{=}NNH_2$ and $(Fl{=}N\text{+}_2$ upon acidification, (4) reduction of FlN_2 in the presence of a strong proton donor, e.g., hexafluoroisopropanol (HFIP), results in protonation at C_9 of $FlN_2^{\cdot-}$ affording FlH_2 as the major product, and (5) $Fl{=}NNH^-$ and FlH^- both initiate azine formation, but the extent of reaction by these chain processes is minor compared to that of $FlN_2^{\cdot-}$, and they do not proceed through the unidentified dimeric dianion.[9]

The two systems which have been discussed, Ph_2CN_2 and FlN_2, each afford several electroactive intermediates and products. In order to distinguish among the many processes that are observed for the electroreductions of Ph_2CN_2 and FlN_2, separate electrochemical studies of all proposed electroactive intermediates and products were deemed necessary. In previous papers from this laboratory the redox behavior of the carbanion intermediates (Ph_2CH^- and FlH^-),[15] the hydrocarbon (FlH_2),[16] the hydrazones ($Ph_2C{=}NNH_2$, $Fl{=}NNH_2$, $Ph_2CHNHN{=}CPh_2$, and $FlHNH{=}Fl$)[17] and the azines ($Ph_2C{=}NN{=}CPh_2$ and $Fl{=}NN{=}Fl$)[17] have been reported. In chapter IV species which arise from the stepwise reduction of the simple hydazones, $Ph_2C{=}NNH_2$ and $Fl{=}NNH_2$, are examined. The compounds studied include benzophenone imine ($Ph_2C{=}NH$) and fluorenone imine ($Fl{=}NH$), 9-aminofluorene ($FlHNH_2$), and several N-substituted derivatives of these species.

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1. The term "hypovalent radicals" is used to describe a neutral or charged radical species containing less than the number of attached substituents found in the uncharged, free radical system normally associated with the central atom in the radical; e.g., triplet H_2C: and HC⁝ are neutral carbon hypovalent radicals.

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AUTHOR: James H. Barnes, Jr.

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( ) a. YES ( ) b. NO

2. Do you believe this research topic is significant enough that it would have been researched (or contracted) by your organization or another agency if AFIT had not?

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( ) a. HIGHLY SIGNIFICANT ( ) b. SIGNIFICANT ( ) c. SLIGHTLY SIGNIFICANT ( ) d. OF NO SIGNIFICANCE

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ABSTRACT

The redox behavior of several nitrogen containing derivatives of fluorenone and benzophenone has been studied. In this continuation of the study of possible precursors to carbene anion radicals, diphenyldiazomethane (Ph_2CN_2) has been studied in acetonitrile (AN) containing Me_4NPF_6 (saturated) as the supporting electrolyte. This was done to confirm that the lifetime of the anion radical ($Ph_2CN_2^{\cdot}$) is less than 1 ms in this electrolyte system. Parker and Bethell have recently reported that electroreduction of Ph_2CN_2 in AN-Me_4NPF_6 (saturated) at a hanging mercury drop electrode is electrochemically reversible at T = 8°C and v = 100 V/s. We have shown that their interpretation is in error, and that it is an artifact of unrecognized adsorption effects on the mercury electrode. The results reported here are consistent with previous findings using platinum as the cathode, i.e., the $Ph_2CN_2^{\cdot}$ initially formed undergoes rapid loss of molecular nitrogen ($t^{1/2}$ ⊖ < on = 1 ms) to yield the carbene anion radical.

Other compounds reported are fluorenone imine (Fl=NH), N-phenylfluorenone imine (Fl=NPh), benzophenone imine (Ph_2C=NH), 9-aminofluorene ($FlHNH_2$) and 9-N,N-dimethylaminofluorene ($FlHNMe_2$). The imines have been shown to be reduced in two successive one-electron steps in aprotic media, first to the anion radical which is stable on the cyclic voltammetric time scale and then to the unstable dianion. However, on the coulometric time scale the anion radical was also shown to undergo a series of reactions leading to the amine in high yield. The reduction of the amines to their anion radicals was rendered irreversible by decomposition to FlH· and the amide anion.

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II. EXPERIMENTAL

Electrochemical instrumentation. Cyclic voltammetric and chronoamperometric experiments were performed with three-electrode potentiostats which incorporated circuits for electronic correction of ohmic potential loss between the reference and working electrodes.[1] Control of the potentiostat and the acquisition and processing of chronoamperometric data were performed with a laboratory computer (LSI 11/2, ADAC System 2000). The three-electrode potentiostat which was used for the exhaustive, controlled-potential electrolyses has also been described.[2]

Cells, electrodes, and electrolysis procedures. All electrochemical experiments were performed on an all-glass vacuum line. The solvent was transferred into the cell on the vacuum line by trap-to-trap distillation. Traces of oxygen, if present, were removed by several freeze-pump-thaw cycles. To bring the cell up to atmospheric pressure, the system was filled with helium. A positive pressure of helium was maintained while the reference electrode was being transferred into the cell. Slush baths (8, 0, -22, and -51°C), were used to maintain the cells at a constant temperature when studies were performed at temperatures other than room temperature. These were prepared using liquid nitrogen and the appropriate liquid following the directions given by Shriver.[3]

Platinum, vitreous carbon, and hanging mercury drop electrodes were used. The area of the platinum planar button electrode which was used in all chronoamperometric and some cyclic voltammetric experiments was 0.25 cm^2 while the area of the planar vitreous carbon electrode[4] which was used in some cyclic voltammetric experiments was 0.20 cm^2. The platinum electrode is a commercially available inlay (Corning). These electrodes are washed between experiments with trichloroethylene, 95% ethanol, and then dried in an oven at 90°C. They were occasionally polished (approximately once every two weeks) when the broad, reversible couple near 0 V in DMF-0.1 F (n-Bu)$_4$NClO$_4$ exceeded $\simeq 2\ \mu A$ (or $\simeq 8\ \mu A\ cm^{-2}$) at a scan rate of 0.2 V/s. All potentials listed are with respect to a cadmium amalgam which is in contact with a dimethylformamide solution that is saturated with both sodium chloride and cadmium chloride (Type A-III).[5] The potential of this electrode is -0.75 V vs. SCE.[6] Dual reference electrodes were used in all rapid scan cyclic voltammetric and chronoamperometric experiments.[7] The second reference electrode, which was a platinum wire in series with a 0.1 μf capacitor, was placed in parallel with the cadmium amalgam electrode.

The extent of large-scale electrolyses was monitored periodically by cyclic voltammetry. At the conclusion of the experiment, the electrolysis mixture was protonated in a dry helium atmosphere with an appropriate proton donor (e.g., diethyl malonate). The mixtures were then analyzed directly by high performance liquid chromatography (HPLC).

Chromatography. The products of the electrolyzed solutions were separated by HPLC using a 6.35-mm diameter, 25-cm length stainless steel column packed with LiChrosorb RP8 or LiChrosorb RP18, 10-μm mean particle size. The eluting solvent was a mixture of methanol and water; the ratio of the mixture and the flow rate (1-3 mL/min) were dependent upon the nature of the products being analyzed (Table II-1). A Waters Associates Inc. Model 6000A pump was used together with a Valco sample injector valve. The detector was a Schoeffel Instrument Corp., model SF-770 UV-VIS spectrophotometer; the wavelength used was 254 nm. Calibration curves for standards of all products were constructed daily.

Chemicals. N,N-Dimethylformamide (Burdick and Jackson) was purified by passage through a column of alumina (80-200 mesh, Brockman activity 1, activated at 600°C overnight) and was collected over a mixture of activated Davison 4A molecular sieves and alumina. This procedure was carried out in a dry, nitrogen-filled glovebag. Acetonitrile (Burdick and Jackson) was purified by the procedure of Walter and Ramaley.[8]

Whether synthesized (Table II-2) or purchased from a commercial supplier, all compounds studied were further purified by established procedures. Purity was checked by a melting point determination and/or by chromatography. 9-Aminofluorene was prepared from the hydrochloride (Aldrich Chemical Company). Heat and light-sensitive reagents were stored at -10°C in well-sealed brown glass bottles. All remaining reagents, except for solvents and supporting electrolytes, were stored in a desiccator over phosphorus pentoxide. Tetrabutylammonium perchlorate (Southwestern Analytical Chemicals), and tetramethylammonium hexafluorophosphate (Aldrich) were used as the supporting electrolytes. These salts were stored in a vacuum oven at 60°C with phosphorus pentoxide as the desiccant.

TABLE II-1. HPLC Eluting Solvent Systems

Compound	%MeOH	%H_2O	Buffer
Benzophenone Imine	45	55	0.085 M Formic Acid 0.015 M Sodium Formate
Diphenylmethylamine	45	55	↓
Benzophenone	55	45	↓
Fluorenone Imine	65	35	0.09 M Sodium Acetate 0.01 M Acetic Acid
9-Aminofluorene	65	35	↓
Fluorenone	65	35	↓
N,N-Dimethyl-9-aminofluorene	80	20	↓
N-Phenylfluorenone Imine	80	20	↓
Bifluorenylidene	90	10	
Fluorenone Azine	90	10	

TABLE II-2. Compounds Synthesized for Study and the References for the Synthetic Procedures

Compound	Reference No.
Benzophenone Imine	9
Diazodiphenylmethane	10
Fluorenone Imine	11
N-Phenylfluorenone Imine	12
N,N-Dimethyl-9-aminofluorene	13

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III. ELECTROREDUCTION OF DIPHENYLDIAZOMETHANE IN ACETONITRILE AT A HANGING MERCURY DROP ELECTRODE

INTRODUCTION

The electrochemical reduction of diphenyldiazomethane (Ph_2CN_2) in N,N-dimethylformamide (DMF) containing 0.1 M ($\underline{n}$-Bu)$_4$NClO$_4$ at a platinum cathode was reported to involve the intermediacy of both $Ph_2CN_2^{\cdot -}$ and $Ph_2C^{\cdot -}$.[1,2] Although $Ph_2CN_2^{\cdot -}$ was not directly observed on the cyclic voltammetric time scale, its presence was inferred by the formation of $Ph_2C{=}NNH_2$ when electroreduction of Ph_2CN_2 was effected in the presence of added proton donors. From these and other results, $Ph_2CN_2^{\cdot -}$ was concluded to react principally by rapid loss of molecular nitrogen to give the carbene anion radical, $Ph_2C^{\cdot -}$. The principal reaction products, $Ph_2C{=}N{-}N{=}CPh_2$ and Ph_2CH_2, were proposed to arise by a chain reaction in which Ph_2CH^- is the chain-carrying species (eqs. III-1 thru -9):

$$Ph_2CN_2 + e^- \longrightarrow Ph_2CN_2^{\cdot -} \qquad \text{(III-1)}$$

$$Ph_2CN_2^{\cdot -} \begin{cases} \xrightarrow{HA,\,e^-} Ph_2C{=}N\bar{N}H + A^- & \text{(III-2)} \\ \xrightarrow{-N_2} Ph_2C^{\cdot -} \xrightarrow{H^+,\,e^-} Ph_2CH^- & \text{(III-3)} \end{cases}$$

$$Ph_2CH^- + Ph_2CN_2 \longrightarrow Ph_2CH\bar{N}N{=}CPh_2 \qquad \text{(III-4)}$$

$$B + Ph_2CH\bar{N}N{=}CPh_2 \longrightarrow BH^+ + Ph_2C{=}N{-}N{=}CPh_2^{\,2-} \qquad \text{(III-5)}$$

$$Ph_2C{=}N{-}N{=}CPh_2^{\,2-} + 2\,Ph_2CN_2 \longrightarrow Ph_2C{=}N{-}N{=}CPh_2 + 2\,Ph_2CN_2^{\cdot -} \qquad \text{(III-6)}$$

$$Ph_2C{=}N\bar{N}H + Ph_2CN_2 \longrightarrow Ph_2C{=}N\bar{N}CHPh_2 + N_2 \qquad \text{(III-7)}$$

$$Ph_2C{=}N\bar{N}H + HA \longrightarrow Ph_2C{=}NNH_2 + A^- \qquad \text{(III-8)}$$

$$Ph_2\bar{C}H + HA \longrightarrow Ph_2CH_2 + A^- \qquad \text{(III-9)}$$

(where B = Ph_2CH^-, $Ph_2C^{\cdot-}$ or $Ph_2CN_2^{\cdot-}$, and HA = $Ph_2CH\bar{N}N{=}CPh_2$ or $(\underline{n}\text{-Bu})_4N^+$)

The stability of $Ph_2CN_2^{\cdot-}$ and its principal reaction mode (eq. III-3) have been questioned.[3] Whereas we found that $Ph_2CN_2^{\cdot-}$ was too unstable ($\underline{t}^{1/2}$ < 1 ms) to give a discernible anodic peak on the reverse, positive-going sweep in a cyclic voltammetric experiment under all conditions examined ($-51^\circ C \leq \underline{T} \leq 23^\circ C$; 0.5 V/s $\leq \underline{v} \leq$ 100 V/s; DMF, CH_3CN, and C_3H_7CN; $(\underline{n}\text{-Bu})_4NClO_4$ and/or Me_4NPF_6),[1,2] Parker and Bethell[3] claim that Ph_2CN_2 is reduced reversibly at a mercury cathode in acetonitrile containing Me_4NPF_6. We will demonstrate in this chapter that Parker and Bethell's observation is an artifact of their use of a mercury electrode surface for their electrochemical studies, and that their "reversible couple" is a fortuitous combination of two different redox processes.

RESULTS AND DISCUSSION

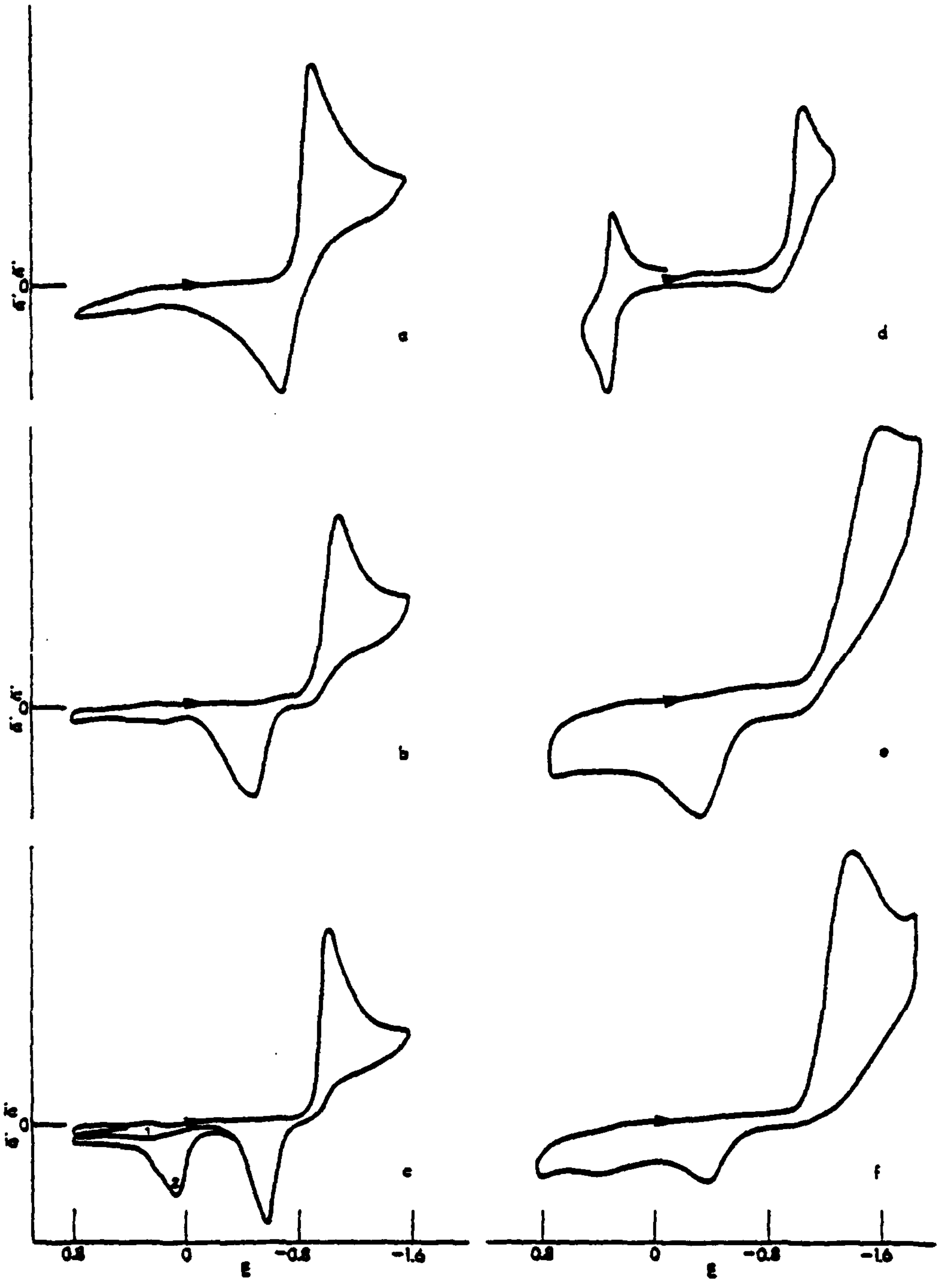
The cyclic voltammetric behavior of Ph_2CN_2 at a hanging mercury drop electrode is illustrated in Figure III-1, a-d. Under the conditions specified by Parker and Bethell for the observance of the reversible reduction of Ph_2CN_2 to $Ph_2CN_2^{\cdot-}$ ($\underline{T} = 8^\circ C$, a scan rate of 100 V/s, and a saturated CH_3CN solution of Me_4NPF_6), a cyclic voltammogram is obtained which resembles that expected for an electrochemically reversible one-electron process (Figure III-1a). However, although the separation of 60 mV for $\underline{E}_p - \underline{E}_{p/2}$ for the cathodic wave is consistent with this interpretation, the 220 mV separation between the anodic and cathodic peak potentials greatly exceeds the expected value of approximately 60 mV. The fact that $Ph_2CN_2^{\overline{\cdot}}$ is not reversibly formed becomes obvious when the temperature is lowered. At -37°C and a scan rate of 100 V/s, the shape of the anodic peak clearly reflects the effect of adsorption on the mercury surface. In addition, the separation between the anodic and cathodic peak potentials has increased to approximately 550 mV (Figure III-1b). Kinetic behavior also becomes evident as the scan rate is decreased. At -37°C and a scan rate of 20 V/s, an adsorption peak that occurs at the same potential as that for the irreversible oxidation of $Ph_2CH\overline{N}N{=}CPh_2$ appears near 0.1 V on the second positive-going half cycle (Figure III-1c).

In addition to the claim by Parker and Bethell that $Ph_2CN_2^{\overline{\cdot}}$ can be observed directly by cyclic voltammetry in CH_3CN in the presence of Me_4N^+, they reported that the cathodic peak potential for the reduction of Ph_2CN_2 is unaffected by the presence of electroinactive diethyl malonate (DEM). From this result, these workers concluded that the proton donor is not involved kinetically in the decomposition of $Ph_2CN_2^{\overline{\cdot}}$ under the reaction conditions, and that $Ph_2CN_2^{\overline{\cdot}}$ must undergo relatively slow, rate-determining hydrogen atom abstraction from acetonitrile. In our experiments, added DEM has a pronounced effect on the reduction of Ph_2CN_2 in CH_3CN as shown by comparing Figures III-1a and III-1d, the latter containing a 22-fold excess of DEM. The addition of DEM essentially eliminates the anodic peak at -0.7 V on the reverse, positive-going sweep, and a reversible couple appears near 0.4 V. Since this same couple can be made to appear by scanning in the positive-going direction from an initial potential of 0 V if a base such as Me_4NOH is added to a solution of DEM in CH_3CN-Me_4NPF_6 (saturated), the conjugate base of DEM must be generated as a result of the electroreduction of Ph_2CN_2 in the presence of DEM. The effects of temperature and proton donor not only disprove Parker and Bethell's assignment of the anodic peak near -0.7 V as being due to the reoxidation of $Ph_2CN_2^{\overline{\cdot}}$, but it also invalidates their attempt to relate the disappearance of this anodic adsorption peak to the kinetics of $Ph_2CN_2^{\overline{\cdot}}$ decomposition.

In contrast, when the electroreduction of Ph_2CN_2 is effected on a platinum electrode surface under these conditions ($\underline{T}$ = 8°C, scan rate of 100 V/s, and CH_3CN-Me_4NPF_6 (saturated)), no adsorption is apparent and the cyclic voltammetric results are consistent with the interpretation which we presented previously for the reduction of Ph_2CN_2 in DMF.[1,2] As evidenced by the cyclic voltammogram in Figure III-le, the reduction of Ph_2CN_2 on platinum is chemically irreversible at 8°C at our maximum scan rate of 100 V/s. Although the absence of an anodic wave for the oxidation of $Ph_2CN_2^{\overline{\cdot}}$ precludes a kinetic study of $Ph_2CN_2^{\overline{\cdot}}$ decomposition, it does establish a maximun half-life of 1 ms for $Ph_2CN_2^{\overline{\cdot}}$.[4] The only anodic wave discernible at this scan rate occurs near -0.35 V and is assigned to the irreversible oxidation of Ph_2CH^-, the observed reaction product of $Ph_2CN_2^{\overline{\cdot}}$.[2] The anodic peak for Ph_2CH^- is kinetically controlled and decreases in relative magnitude as the scan rate is decreased (Figure III-1f). Concomitantly, an irreversible anodic peak appears near 0.2 V that is due to the oxidation of the intermediate product, $Ph_2CH\bar{N}N{=}CPh_2$, formed when Ph_2CH^- couples with Ph_2CN_2. The two principal products that were obtained by a coulometric reduction of Ph_2CN_2 at a platinum cathode in CH_3CN- Me_4NPF_6 (saturated) are $Ph_2C{=}N{-}N{=}CPh_2$ (42%) and Ph_2CH_2 (57%).

FIGURE III-1

Cyclic voltammograms for the reduction of Ph_2CN_2 in CH_3CN under the following conditions: (a) $\underline{T}$ = 8°C, $\underline{v}$ = 100 V/s, Me_4NPF_6 (saturated), and hanging mercury drop electrode (HMDE); (b) $\underline{T}$ = -37°C, $\underline{v}$ = 100 V/s, Me_4NPF_6 (saturated), and HMDE; (c) $\underline{T}$ = -37°C, $\underline{v}$ = 20 V/s, Me_4NPF_6 (saturated), and HMDE; (d) $\underline{T}$ = 8°C, $\underline{v}$ = 100 V/s, Me_4NPF_6 (saturated), DEM (89 m$\underline{M}$), and HMDE; (e) $\underline{T}$ = 8°C, $\underline{v}$ = 100 V/s, Me_4NPF_6 (saturated), and planar platinum electrode (0.25 cm^2); and (f) $\underline{T}$ = 8°C, $\underline{v}$ = 20 V/s, Me_4NPF_6 (saturated), and planar platinum electrode.



i_c
0
i_a
a
d
b
e
1
2
c
f
0.8
0
-0.8
-1.6
E

CONCLUSIONS

We suspect that Parker and Bethell's use of mercury may have contributed to the misinterpretation by these workers that $Ph_2CN_2^{\overline{\cdot}}$ has an appreciable lifetime in CH_3CN. The formation of organomercurials when mercury is used as the electrode material is well known (e.g., $(Ph_2CH_2)_2Hg$ formation when Ph_2CH_2Br is reduced at a mercury cathode[5]) and may account for the anodic wave that appears near -0.7 V at 8°C in Figure III-1a. A specific possibility is that Ph_2CH^- is oxidized to $Ph_2CH^{\cdot}$ and that this radical then rapidly reacts with the mercury surface to form an organomercurial species. The effect of this follow-up reaction would be to shift the Ph_2CH^- anodic wave to more negative potential.[4] Since the cathodic peak potential for the irreversible reduction of Ph_2CN_2 will be shifted negatively by decreasing temperature, Parker and Bethell perhaps arrived at a fortuitous set of conditions in which the irreversible reduction of Ph_2CN_2 and the irreversible oxidation of Ph_2CH^- in the presence of mercury appeared to constitute a chemically reversible system.

It is important to note that our coulometric and product data preclude reaction pathways which involve extensive hydrogen atom abstraction by anion radical intermediates. For example, the electroreduction of Ph_2CN_2 in DMF-0.1 F (n-Bu)$_4$NClO$_4$ gives an n value of 0.30 and a product distribution of 87% $Ph_2C{=}N{-}N{=}CPh_2$, 1% $Ph_2C{=}O$, 9% Ph_2CH_2, 2% $Ph_2CHNHN{=}CPh_2$ and 0.6% $Ph_2C{=}NNH_2$.[2] If either $Ph_2CN_2^{\overline{\cdot}}$ or $Ph_2C^{\overline{\cdot}}$ were to hydrogen atom abstract, these hydrogens must ultimately be removed as protons from the coupled intermediate, $Ph_2CH\bar{N}N{=}CPh_2$, by the electrogenerated bases $Ph_2C^{\overline{\cdot}}$, Ph_2CH^-, $Ph_2C{=}NNH^-$, and $Ph_2CH\bar{N}N{=}CPh_2$ (see eqs. III-1 thru III-9). Because the combined yields of the last three products is less than 12% under these conditions, the anion radicals $Ph_2CN_2^{\overline{\cdot}}$ and $Ph_2C^{\overline{\cdot}}$ must instead proton abstract from $Ph_2CH\bar{N}N=CPh_2$ (eq. III-5). Since Ph_2CH^-, not $Ph_2C=NNH^-$, is the first observable electroactive intermediate in the reduction of Ph_2CN_2, we conclude that $Ph_2CN_2^{\overline{\cdot}}$ reacts principally by rapid loss of nitrogen, and that Ph_2CH^- is formed via the intermediacy of the carbene anion radical, $Ph_2C^{\overline{\cdot}}$, as shown in eq. III-3.

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IV. THE ELECTROREDUCTION OF FLUORENONE IMINE, N-PHENYLFLUORENONE IMINE, BENZOPHENONE IMINE, 9-AMINOFLUORENE, AND N,N-DIMETHYL-9-AMINOFLUORENE

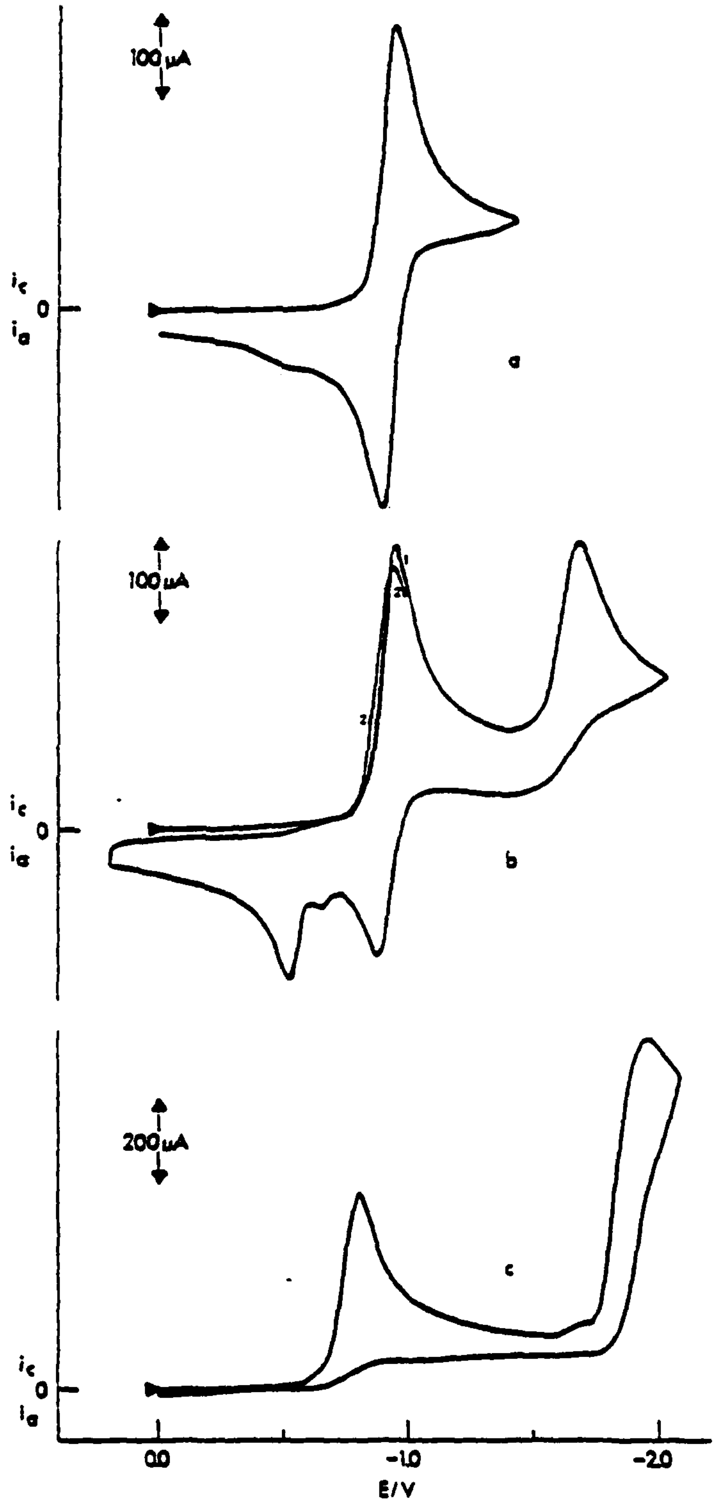
Fluorenone Imine

Cyclic voltammetry. The cyclic voltammetric reduction of $Fl{=}NH$ in DMF-0.1 $\underline{F}$ $(\underline{n}\text{-Bu})_4NClO_4$ at a platinum cathode occurs in successive one-electron steps (Figure IV-1). Although the reduction of $Fl{=}NH$ to $Fl{=}NH^{\cdot -}$ at $\underline{E}_{p,c}$ = -0.92 V is nearly reversible ($\underline{i}_{p,a}/\underline{i}_{p,c} = 0.93$) at the relatively slow scan rate of 0.2 V/s (Figure IV-1a), the reduction of $Fl{=}NH^{\cdot -}$ to $Fl{=}NH^{2-}$ at $\underline{E}_{p,c}$ = -1.68 V occurs irreversibly at all scan rates and temperatures in the range $0.05\ V/s \leq \underline{v} \leq 100\ V/s$ and $-51^{\circ}C \leq \underline{T} \leq 22^{\circ}C$. Reaction of $Fl{=}NH^{2-}$ causes one or more anodic waves, depending on the temperature and scan rate, to appear on the reverse, positive-going sweep. At room temperature (Figure IV-1b), the most prominent of these is assigned to the irreversible oxidation of $FlNH_2^-$ ($\underline{E}_{p,a} = -0.52$ V). $FlNH_2^-$, which would arise if $Fl{=}NH^{2-}$ were to proton abstract (eq. IV-2), has been shown previously[1] to be oxidized irreversibly to give $Fl{=}NH$. The protons that also are formed during the oxidation are then captured by unreacted $FlNH_2^-$.

The $FlHNH_2$ which is formed upon the oxidation of $FlNH_2^-$ has a modest effect on the redox behavior of $Fl{=}NH$ on the second, negative-going scan. Protonation of $Fl{=}NH^{\cdot -}$ by $FlHNH_2$ affords $FlNH_2^{\cdot}$ and $FlNH_2^-$; $FlNH_2^{\cdot}$ is rapidly reduced, either electrochemically or chemically, by unreacted $Fl{=}NH^{\cdot -}$ (eq. IV-3). The protonation of $Fl{=}NH^{\cdot -}$ by $FlHNH_2$ thus facilitates the reduction of

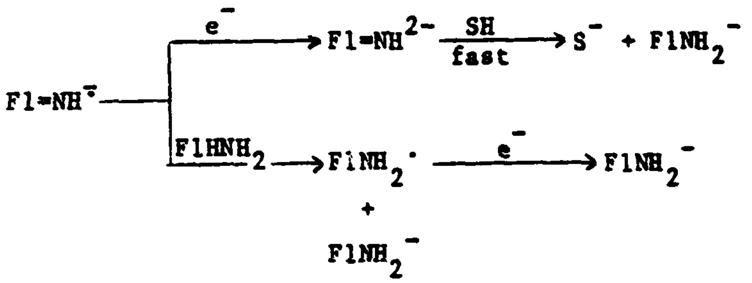
FIGURE IV-1

Cyclic voltammograms of Fl=NH in DMF-0.1 F (n-Bu)$_4$NClO$_4$ at a planar platinum electrode. The scans were initiated at 0 V in the negative-going direction at a rate 0.2 V/s. The temperature was 23°C; (a) 2.41 m$\underline{M}$ Fl=NH; (b) 9.46 m$\underline{M}$ Fl=NH; (c) 3.01 m$\underline{M}$ Fl=NH and 23.41 m$\underline{M}$ diethyl malonate.


100 µA
i_c
0
i_a
a
100 µA
1
2
2
b
200 µA
c
0.0
-1.0
-2.0
E/V

Fl=NH, thereby causing a shoulder to appear on the positive side of the Fl=NH cathodic peak on the second, negative-going scan (Figure IV-1b). Since the concentration of Fl=NH exceeds the concentration of $FlHNH_2$ at the electrode surface, all $FlHNH_2$ which was produced during the positive-going half cycle will be consumed when reduction of Fl=NH is affected on the second, negative-going half cycle. As a result, no cathodic wave for the reduction of $FlHNH_2$ is seen near -1.92 V (vide infra) on the second, negative-going scan.

$$Fl{=}NH + e^- \longrightarrow Fl{=}NH^{\cdot -} \qquad (IV\text{-}1)$$



$$Fl{=}NH^{\cdot -} \xrightarrow{e^-} Fl{=}NH^{2-} \xrightarrow[\text{fast}]{SH} S^- + FlNH_2^- \qquad (IV\text{-}2)$$

$$Fl{=}NH^{\cdot -} \xrightarrow{FlHNH_2} FlNH_2^{\cdot} + FlNH_2^- \qquad FlNH_2^{\cdot} \xrightarrow{e^-} FlNH_2^- \qquad (IV\text{-}3)$$

Coulometry. The controlled potential electrolysis of Fl=NH was effected at a potential ($E_{applied}$ = -1.0 V) which was sufficiently negative so as to reduce Fl=NH to its anion radical, but not so negative so as to cause reduction of $Fl{=}NH^{\cdot -}$ to $Fl{=}NH^{2-}$. HPLC analysis of a solution in which electrolysis was terminated arbitrarily at the point of 1.5 electrons per molecule of Fl=NH showed that 72% of the Fl=NH which was originally present had been converted into $FlHNH_2$ (Table IV-2). This result is consistent with a nominal n value of 2.0 for the reduction of Fl=NH to $FlHNH_2$.

While $Fl{=}NH^{\cdot -}$ is quite stable on the cyclic voltammetric time scale, its reaction on the coulometric time scale is relatively rapid. Periodic monitoring of the electrolysis experiment by cyclic voltammetry showed that the Fl=NH peak height remains almost constant for $n \leq 1.0$, and then decreases

TABLE IV-1. Coulometric Data and Product Studies for the Controlled Potential, Electrolytic Reductions of Fluorenone and Benzophenone Imines

Entry No.	Compound	Conc., m*M*	*E*applied, V	*n*	Proton Donor; Conc., m*M*	Products, % yield			
						$R_2C{=}NH$	R_2CHNH_2	$R_2C{=}O$	R_2CH_2
1.	Fl=NH	4.43	-1.0	1.5		21	72	2	-
2.	Fl=NH	3.01	-0.9	2.3	DEM; 23.4	7	82	2	12
3.	$Ph_2C{=}NH$	6.51	-1.5	2.0		2.5	97	1	-
4.	$Ph_2C{=}NH$	9.63	-1.3	2.0	TFE; 101.1	13	87	2	-

linearly to zero in the range $1.0 \leq \underline{n} \leq 2.0$. Concomitantly, the peak height for the reduction of $Fl{=}NH^{\overline{\cdot}}$ to $Fl{=}NH^{2-}$ decreases linearly to zero as $\underline{n}$ approaches 1. If $\underline{n} > 1$, a cathodic wave for the reduction of $FlHNH_2$ is also present at −1.92 V.

The fact that the magnitude of the Fl=NH cathodic wave remains constant for $\underline{n} \leq 1$ also requires that $FlNH_2^-$ rather rapidly abstract a proton from a component of the solvent-electrolyte system. A constant peak height for Fl=NH reduction is then predicted as long as $[Fl{=}NH] \geq [FlHNH_2]$, and the sum of the instantaneous concentrations of Fl=NH and $FlHNH_2$ equals the initial concentration of Fl=NH. The pathway by which $Fl{=}NH^{\overline{\cdot}}$ reacts cannot be ascertained from these data, but presumably it involves either disproportionation of $Fl{=}NH^{\overline{\cdot}}$ or a half-regeneration mechanism in which $Fl{=}NH^{\overline{\cdot}}$ is protonated by a component of the solvent-electrolyte system, and the resulting $FlNH_2^{\cdot}$ is reduced by unreacted $Fl{=}NH^{\overline{\cdot}}$.

Chronoamperometry. Inspection of the cyclic voltammogram of Fl=NH (Figure IV-1b) shows that the magnitude of the cathodic peak for the reduction of $Fl{=}NH^{\overline{\cdot}}$ to $Fl{=}NH^{2-}$ is approximately two-thirds of that for the reduction of Fl=NH to $Fl{=}NH^{\overline{\cdot}}$. Since $\underline{i}_{p,a}/\underline{i}_{p,c} = 0.93$ at $\underline{v} = 0.2$ V/s for the reduction of Fl=NH to $Fl{=}NH^{\overline{\cdot}}$ (Figure IV-1a), the possibility that the smaller-than-expected peak height for the reduction of $Fl{=}NH^{\overline{\cdot}}$ to $Fl{=}NH^{2-}$ may be due to causes other than a follow-up reaction involving $Fl{=}NH^{\overline{\cdot}}$ was examined. First, $Fl{=}NH^{2-}$ may be reacting with Fl=NH, e.g., proton transfer, to give a product or products which are electroinactive at the potential at which $Fl{=}NH^{\overline{\cdot}}$ is reduced to $Fl{=}NH^{2-}$. Second, if the rate of the follow-up reaction involving $Fl{=}NH^{2-}$ is very rapid, the $Fl{=}NH^{\overline{\cdot}}$ cathodic peak height will be a function of the transfer coefficient for heterogeneous electron transfer. In order to test the merit of these possibilities, the stepwise reduction of $Fl{=}NH$ to $Fl{=}NH^{2-}$ was examined by single potential step chronoamperometry. The reduction of $Fl{=}NH$ to $Fl{=}NH^{\cdot-}$ ($\underline{E}_{applied}$ = -1.40 V) afforded $\underline{it}^{1/2}/\underline{c}$ = 41 ± 3 $\mu A \cdot s^{1/2} \cdot m\underline{M}^{-1}$ for the time range 8 ms $\leq \underline{t} \leq$ 4s. When the potential instead was stepped sufficiently negative so as to effect the reduction of $Fl{=}NH$ to $Fl{=}NH^{2-}$ ($\underline{E}_{applied}$ = -1.95 V), the values for $\underline{it}^{1/2}/\underline{c}$ were approximately 1.8 times larger than the corresponding values at the less negative potential. In order to relate these values to the number of electrons involved, the reduction of fluorenone ($Fl{=}O$) to its stable anion radical was studied under similar conditions. If it is assumed that the diffusion coefficients of $Fl{=}NH$ and $Fl{=}O$ are equal, then the $\underline{it}^{1/2}/\underline{c}$ value of 37 $\mu A \cdot s^{1/2} \cdot m\underline{M}^{-1}$ that was obtained for the one-electron reduction of $Fl{=}O$ indicates that the number of electrons transferred in the first and second steps of the reduction of $Fl{=}NH$ are approximately 1.1 and 0.9 (2.0 overall), respectively. These results are consistent with a minor reaction channel involving the slow protonation of $Fl{=}NH^{\cdot-}$, a cathodic peak shape for the reduction of $Fl{=}NH^{\cdot-}$ to $Fl{=}NH^{2-}$ which is controlled by slow electron transfer, and little, if any, reaction of $Fl{=}NH^{2-}$ with $Fl{=}NH$ to give an electroinactive product.

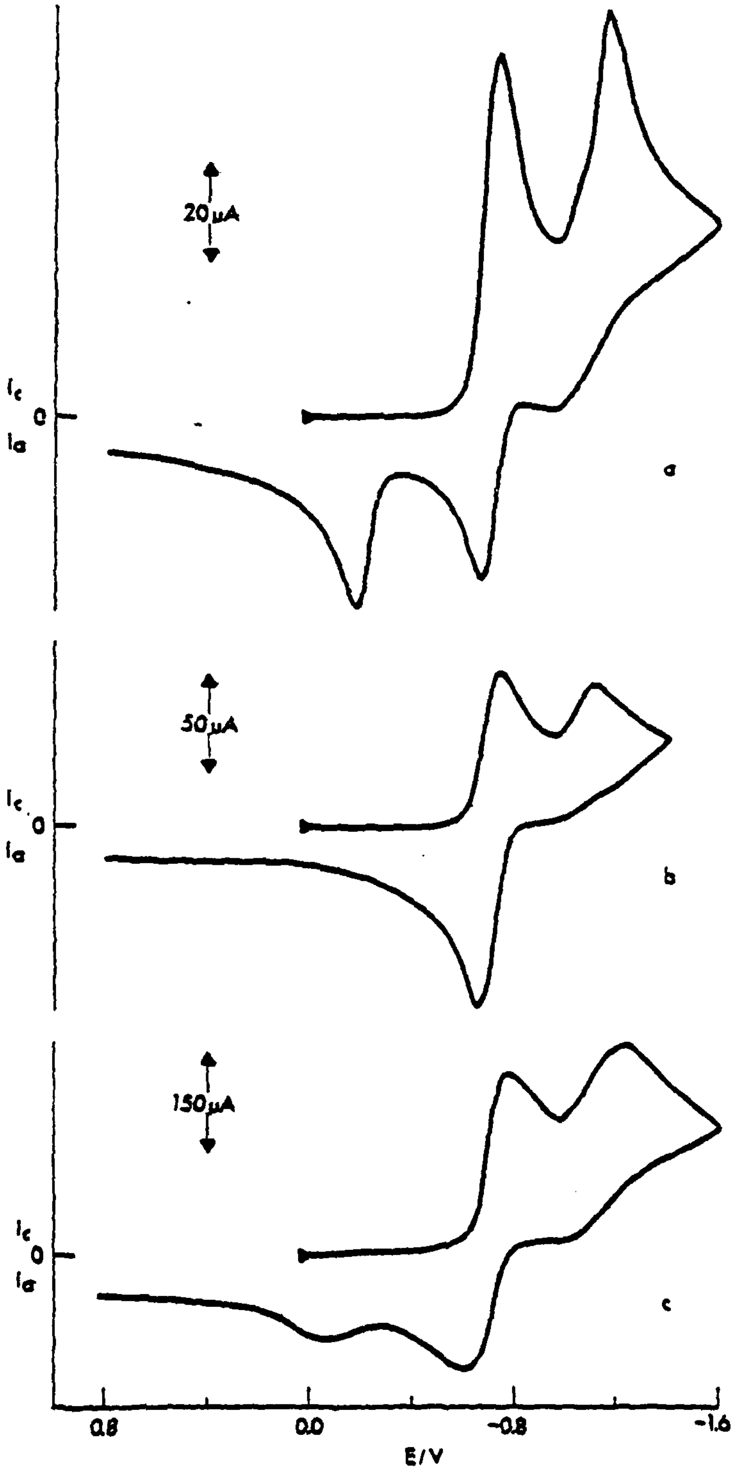
Effect of diethyl malonate (DEM). The addition of DEM, a weak proton donor, causes the cyclic voltammetric peak height for the reduction of $Fl{=}NH$ to $Fl{=}NH^{\cdot-}$ ($\underline{E}_{p,c}$ = -0.92 v) to increase approximately 1.8 times, eliminates the cathodic peak attributed to the reduction of $Fl{=}NH^{\cdot-}$ to $Fl{=}NH^{2-}$ at -1.6 V, causes a new peak to appear near -1.92 V which is due to the concomitant reduction of $FlHNH_2$ and its two-electron reduction product, fluorene (FlH_2), and eliminates all anodic peaks on the positive-going half cycle (Figure IV-1c). The chronoamperometric $\underline{n}$ value which was obtained at a potential ($\underline{E}$ = - 1.35 V) that was sufficiently negative so as to reduce $Fl{=}NH$ to $Fl{=}NH^{\overline{\cdot}}$, but not so negative so as to cause the reduction of $Fl{=}NH^{\overline{\cdot}}$ to $Fl{=}NH^{2-}$, is diffusion controlled and equal to 2 in the time range $8\ ms \le \underline{t} \le 8\ s$. This result is consistent with rapid protonation of all anionic intermediates and the formation of $FlHNH_2$ as the final product. Product studies of a partially electrolyzed solution confirmed that $FlHNH_2$ was the principal product (85% relative yield) (Table IV-1, entry 2). Minor amounts of FlH_2 and $Fl{=}O$ were also found. The former species is the expected two-electron reduction product of the more difficultly reduced $FlHNH_2$ (*vide infra*), while the latter species is expected if fluorenyl anions are formed in the presence of adventitious oxygen.[2]

Comparison of the redox behavior of Fl=NH and Fl=NPh. Inspection of Figure IV-1b will show that reduction of $Fl{=}NH^{\overline{\cdot}}$ to $Fl{=}NH^{2-}$ affords a relatively large anodic peak for the oxidation of $FlNH_2^-$ at -0.52 V and a smaller, unidentified anodic peak at -0.62 V. The latter peak shifts positively with increasing scan rate, merging with the $FlNH_2^-$ anodic peak at scan rates in excess of 5 V/s at both room temperature and -51°C.

The possibility that a small, but discernible, amount of electrogenerated $Fl{=}NH^{2-}$ reacts with $Fl{=}NH$ to give $FlNH_2^-$ and $Fl{=}N^-$ and that the latter species is oxidized at -0.62 V was examined. In order to eliminate the possibility of proton transfer, the reduction of the N-substituted fluorenone imine, $Fl{=}NPh$, was studied in the presence and absence of potassium tert-butoxide (K-$\underline{t}$-BuO). When electroreduction of $Fl{=}NPh$ was effected in DMF-0.1 $\underline{F}$ $(\underline{n}\text{-}Bu)_4NClO_4$ at a

FIGURE IV-2

Cyclic voltammograms of Fl=NPh in DMF-0.1 F $(\underline{n}\text{-Bu})_4ClO_4$ at a planar platinum electrode. The scans were initiated at 0 V in the negative-going direction at rates of (a) 0.2 V/s, (b) 0.2 V/s, and (c) 5.0 V/s. The temperature was 23°C. (a) 9.46 mM Fl=NPh; (b) 9.46 mM Fl=NPh and 30 mM K-t-BuO; (c) 9.46 mM Fl=NPh and 30 mM K-t-BuO.


20 μA
50 μA
150 μA
I_c
0
I_a
a
b
c
0.8
0.0
-0.8
-1.6
E/V

platinum electrode, two anodic waves, corresponding to the oxidation of $\text{Fl=NPh}^{\overline{\cdot}}$ ($\underline{E}_{p,a}$ = -0.67 V) and FlNHPh^{-} ($\underline{E}_{p,a}$ = -0.18 V), were observed on the reverse positive-going sweep (Figure IV-2a). However, when K-$\underline{t}$-BuO was added in excess, the oxidation of FlNHPh^{-} occurred in either one or two steps, depending upon the sweep rate. At scan rates less than approximately 1 V/s, the anodic peak ascribed to the oxidation of FlNHPh^{-} ($\underline{E}_{p,a}$ = -0.18 V) disappeared while the anodic peak ascribed to the oxidation of $\text{FlNPh}^{\overline{\cdot}}$ nearly doubled in magnitude (Figure IV-2b). At scan rates in excess of 1 V/s, the anodic peak for FlNHPh^{-} reappeared and grew in relative magnitude at the expense of the $\text{Fl=NH}^{\overline{\cdot}}$ anodic peak with increasing scan rate (Figure IV-2c). The anodic peaks were approximately equal in magnitude under these solution conditions when the scan rate exceeded 50 V/s.

The kinetically controlled cyclic voltammetric behavior of FlNHPh^{-} and $\text{Fl=NPh}^{\overline{\cdot}}$ in the presence of added base must be due to electrocatalysis. The concomitant oxidation of an anion radical and the corresponding anion has ample precedent, e.g., $\text{Fl=O}^{\overline{\cdot}}$ and FlOH^{-} [3] and the conjugate base of a hydroquinone, QH^{-}, and $\text{Q}^{\overline{\cdot}}$, [4] and would occur if Fl=NPh were to accept an electron from the more-difficultly-oxidized FlNHPh^{-} in the rate determining step (eq. IV-5).

$$\text{Fl=NPh}^{\overline{\cdot}} - e^{-} \longrightarrow \text{Fl=NPh} \qquad \text{(IV-4)}$$

$$\text{Fl=NPh} + \text{FlNHPh}^{-} \xrightarrow{\text{slow}} \text{Fl=NPh}^{\overline{\cdot}} + \text{FlNHPh}^{\cdot} \qquad \text{(IV-5)}$$

$$\text{FlNHPh}^{\cdot} + \underline{t}\text{-BuO}^{-} \xrightarrow{\text{fast}} \text{Fl=NPh}^{\overline{\cdot}} + \underline{t}\text{-BuOH} \qquad \text{(IV-6)}$$

Electron transfer is then rendered irreversible by the action of the added base, $\underline{t}\text{-BuO}^{-}$, on $\text{FlNHPh}^{\cdot}$ (eq. IV-6). The failure of FlNHPh^{-} to act in the same capacity as $\underline{t}\text{-BuO}^{-}$ is presumably the result of slow proton transfer from $\text{FlNHPh}^{\cdot}$ to FlNHPh^{-}. The relatively slow rate of proton transfer to and from the C_9 center in several fluorene compounds has been noted previously.[1]

Since an anodic peak which is analogous to the one in question did not appear in the Fl=NPh system, attempts were then made to prepare $Fl{=}N^-$ directly from either the addition or electrogeneration of a strong base. $(CH_3)_4NOH$ in methanol acted only as a proton donor toward $Fl{=}NH^{\cdot-}$, and neither K-*t*-BuO nor electrogenerated $PhN{=}NPh^{2-}$ produced any discernible reaction with Fl=NH. When Fl=NH was reduced to $Fl{=}NH^{2-}$ in the presence K-*t*-BuO, the anodic peak assigned to the oxidation of $FlNH_2^-$ was eliminated while the magnitude of the anodic peak at -0.62 V became approximately twice as large as the $FlNH_2^-$ peak in the absence of base. Surprisingly, unlike the Fl=NPh system, the anodic wave for the oxidation of $Fl{=}NH^{\cdot-}$ was not enhanced when Fl=NH was reduced to either $Fl{=}NH^{\cdot-}$ or $Fl{=}NH^{2-}$ in the presence of K-*t*-BuO. The apparent absence of electrocatalysis in the Fl=NH system is puzzling, since the separation between the $Fl{=}NH^{\cdot-}$ ($E_{p,a}$ = -0.92 V) and $FlNH_2^-$ ($E_{p,a}$ = -0.52 V) anodic peaks is approximately 0.1 V less than the corresponding separation of the anodic peaks for $Fl{=}NPh^{\cdot-}$ ($E_{p,a}$ = -0.67 V) and $FlNHPh^-$ ($E_{p,a}$ = -0.18 V).

While these data appear to be consistent with a pathway which involves the strong-base assisted oxidation of $FlNH_2^-$ (eq. IV-7 thru 10), confirmation of the reaction sequence could not be verified by independent experiment.

$$FlNH_2^- \longrightarrow FlNH_2^{\cdot} + e^- \qquad \text{(IV-7)}$$

$$FlNH_2^{\cdot} \xrightarrow[\text{slow}]{FlNH_2^-} FlHNH_2 + Fl{=}NH^{\cdot-} \qquad \text{(IV-8)}$$

$$FlNH_2^{\cdot} \xrightarrow[\text{fast}]{t\text{-BuO}^-} t\text{-BuOH} + Fl{=}NH^{\cdot-} \qquad \text{(IV-9)}$$

$$Fl{=}NH^{\cdot-} \longrightarrow Fl{=}NH + e^- \qquad \text{(IV-10)}$$

If oxidation of $FlNH_2^-$ were facilitated by the presence of a strong base such as either OH^- formed by action of $Fl{=}NH^{2-}$ on adventitious H_2O or added t-BuO$^-$, theory predicts that the $FlNH_2^-$ anodic peak would be shifted in the negative direction because of the increased rate of proton loss from $FlNH_2^{\cdot}$ (eq. IV-7 and -8) and that the $FlNH_2^-$ anodic peak height could be increased by as much as 100%. Although the addition of K-t-BuO to a solution of Fl=NH does cause these changes to occur when Fl=NH is reduced to $Fl{=}NH^{2-}$, the addition of excess K-t-BuO to a solution of $FlHNH_2$ affords only a single anodic peak for the oxidation of $FlNH_2^-$ at its normal potential of -0.52 V. The expected single anodic peak at -0.62 V could be made to arise only by first oxidizing $FlNH_2^-$ to Fl=NH and then reducing the electrogenerated Fl=NH to $Fl{=}NH^{2-}$; no anodic wave at -0.62 was seen in either the Fl=NH or the $FlNH_2^-$ systems unless the reduction of $Fl{=}NH^{\overline{\cdot}}$ to $Fl{=}NH^{2-}$ was first made to occur.

Finally, since the unidentified anodic peak at -0.62 V occurs at the same potential as that for the reversible one-electron oxidation of fluorenone azine dianion , $Fl{=}N{-}N{=}Fl^{2-}$,[5] the possibility that this species may be formed in small amounts when Fl=NH is reduced to $Fl{=}NH^{2-}$ and that $Fl{=}N{-}N{=}Fl^{\overline{\cdot}}$ then catalyzes the oxidation of $FlNH_2^-$ when an added base is present was examined. However, when $Fl{=}N{-}N{=}Fl^{\overline{\cdot}}$ was added in a small amount to a solution of Fl=NH, no apparent change in the cyclic voltammetric behavior occured. Although the reason why electrocatalysis is not observed in the Fl=NH system under these conditions is not clear, the result is consistent with the similar absence of electrocatalytic oxidation of $FlNH_2^-$ by Fl=NH when K-t-BuO has been added (*vide supra*).

Benzophenone Imine ($Ph_2C=NH$)

The cyclic voltammetric behavior of $Ph_2C=NH$ in DMF-0.1 F (n-Bu)$_4$)$NClO_4$ closely resembles that of Fl=NPh. At a scan rate of 5 V/s, clearly defined cathodic peaks corresponding to the nearly reversible reduction of $Ph_2C=NH$ to $Ph_2C=NH^{\overline{\cdot}}$ and the irreversible reduction of $Ph_2C=NH^{\overline{\cdot}}$ to $Ph_2C=NH^{2-}$ are observed at -1.47 V and -1.96 V, respectively, while anodic peaks are assigned to the oxidation of $Ph_2C=NH^{\overline{\cdot}}$ and $Ph_2CNH_2^-$ arise at -1.40 and -0.88 V, respectively, on the reverse, positive-going sweep. When the scan rate is decreased, loss of reversiblity for the $Ph_2C=NH/Ph_2C=NH^{\overline{\cdot}}$ couple occurs, as evidenced by a value of 0.52 for $i_{p,a}/i_{p,c}$ at v = 0.2 V/s. Concomitantly, the relative magnitude of the $Ph_2C=NH$ cathodic wave is increased, with its increase occurring at the expense of the more-negative cathodic wave for the reduction of $Ph_2C=NH^{\overline{\cdot}}$ to $Ph_2C=NH^{2-}$. In addition, the anodic peak assigned to the irreversible oxidation of $Ph_2CNH_2^-$ is no longer discernible at a scan rate of 0.1 V/s. The latter result is consistent with the known instability of benzhydryl anions and their propensity to proton abstract. The former result is consistent with the relatively slow abstraction of a proton from a component of the solvent-supporting electrolyte system by $Ph_2C=NH^{\overline{\cdot}}$ and the subsequent reduction of $Ph_2CNH_2^{\cdot}$ at the applied potential to give $Ph_2C=NH_2^-$. The formation of Ph_2CHNH_2 upon reduction of $Ph_2C=NH$ to its anion radical was confirmed by product studies from controlled potential electrolyses and occurred when reduction was effected in either the presence or absence of an added proton donor (entries 3 and 4, Table IV-1).

9-Aminofluorene ($FlHNH_2$)

Cyclic voltammetry. The cyclic voltammetric reduction of $FlHNH_2$ to $FlHNH_2^{\cdot-}$ ($E_{p,c} = -1.92$ V) is nearly reversible at $T = -51^{\circ}C$ and $v \geq 20$ V/s. As the temperature is increased and/or the scan rate is decreased, the decomposition of $FlHNH_2^{\cdot-}$ first affords two equal-sized, irreversible, anodic processes which appear near -0.48 V and 0.12 V (Figure IV-3a). The more-negative process has been assigned above to the irreversible oxidation of $FlNH_2^-$ to give Fl=NH while the more-positive peak has been shown in earlier work[2] to be due to the irreversible oxidation of 9-fluorenyl anion, FlH^-. As the scan rate is decreased further (Figure IV-3b), the relative magnitude of the $FlNH_2^-$ anodic peak is increased at the expense of the FlH^- anodic peak. Finally, at room temperature and a scan rate of 0.2 V/s, both the reversibility for the reduction of $FlHNH_2$ and the anodic peak for the oxidation of FlH^- disappear. Subsequent negative-going scans show, in addition to the $FlHNH_2$ cathodic peak, a single cathodic peak ($E_{p,c} = -0.84$ V) for the reduction of the Fl=NH which is electrogenerated by the oxidation of $FlNH_2^-$ on the previous positive-going half-cycle. Since the sum of the $FlHNH_2$ and FlH_2 concentrations at the electrode surface exceeds the concentration of electrogenerated Fl=NH, the reduction of Fl=NH on the second negative-going scan occurs in a single, irreversible, two-electron step to regenerate $FlHNH_2$.

Proposed reaction scheme. The scheme described by eqs. IV-11 thru -16 is proposed to account for the kinetically controlled behavior of the $FlHNH_2^{\cdot-}$, $FlNH_2^-$, and FlH^- anodic peaks.

$$FlHNH_2 + e^- \longrightarrow FlHNH_2^{\cdot-} \qquad \text{(IV-11)}$$

$$FlHNH_2^{\cdot-} \xrightarrow{slow} FlH^{\cdot/-} + NH_2^{-/\cdot} \qquad \text{(IV-12)}$$

$$FlHNH_2^{\cdot-} + FlH^{\cdot} \text{ or } NH_2^{\cdot} \longrightarrow FlHNH_2 + FlH^{-} \text{ or } NH_2^{-} \tag{IV-13}$$

$$NH_2^{-} + FlHNH_2 \xrightarrow{fast} NH_3 + FlNH_2^{-} \tag{IV-14}$$

$$FlH^{-} + FlHNH_2 \xrightarrow{K} FlH_2 + FlNH_2^{-} \tag{IV-15}$$

$$FlH_2 + e^{-} \longrightarrow FlH_2^{\cdot-} \tag{IV-16}$$

The reduction of $FlHNH_2$ as a diffusion controlled, overall one-electron step was ascertained by single-potential-step chronoamperometry. Although double-potential-step chronoamperometry established that the decomposition of $FlHNH_2^{\cdot-}$ was first order in this species ($\underline{k} = 0.8\ s^{-1}$ at $-22^{o}C$; see Figure IV-4), it could not be determined unequivocally which fragment of the carbon-nitrogen bond cleavage bears the negative charge (eq. IV-12). The $-/\cdot$ superscript which is written for each of the fragments reflects this uncertainty. However, the chronoamperometric data do require that the radical fragment be reduced by unreacted $FlHNH_2^{\cdot-}$ (eq. IV-13) and that NH_2^{-} rapidly abstract a proton from $FlHNH_2$ (eq. IV-14). The disappearance of the FlH^{-} anodic peak with decreasing scan rate is the result of relatively slow proton transfer from $FlHNH_2$ to electrogenerated FlH^{-} (eq. IV-15) and the subsequent oxidation of the more-readily-oxidized $FlNH_2^{-}$. Because the FlH_2 which is formed in this reaction is also reduced to its relatively stable anion radical at the same potential at which $FlHNH_2$ is reduced,[2] the experimental double-potential-step chronoamperometric data for this process deviate from the theoretical curve for the simple, first order EC model at larger values of time, $\underline{t}$. A more complicated EC model which includes the effect of eqs. IV-15 and -16 was not developed. If the knowledge of the proton transfer rate constant in eq. IV-15 were of interest, a double-potential-step chronoamperometric method which involves the reduction of $FlHNH_2$ on the forward step and the oxidation of both unreacted $FlHNH_2^{\cdot-}$ and $FlNH_2^{-}$ on the reverse step should be amenable experimentally. The value of the equilibrium

FIGURE IV-3

Cyclic voltammograms of $FlHNH_2$ in DMF-0.1 F ($\underline{n}$-Bu)$_4$ClO$_4$ at a spherical platinum electrode. The scans were initiated at 0 V in the negative-going direction at rates of (a) 100 V/s and (b) 5 V/s. Concentration of $FlHNH_2$ is 5.95 mM. The small "2" indicates the second scan in the negative direction.

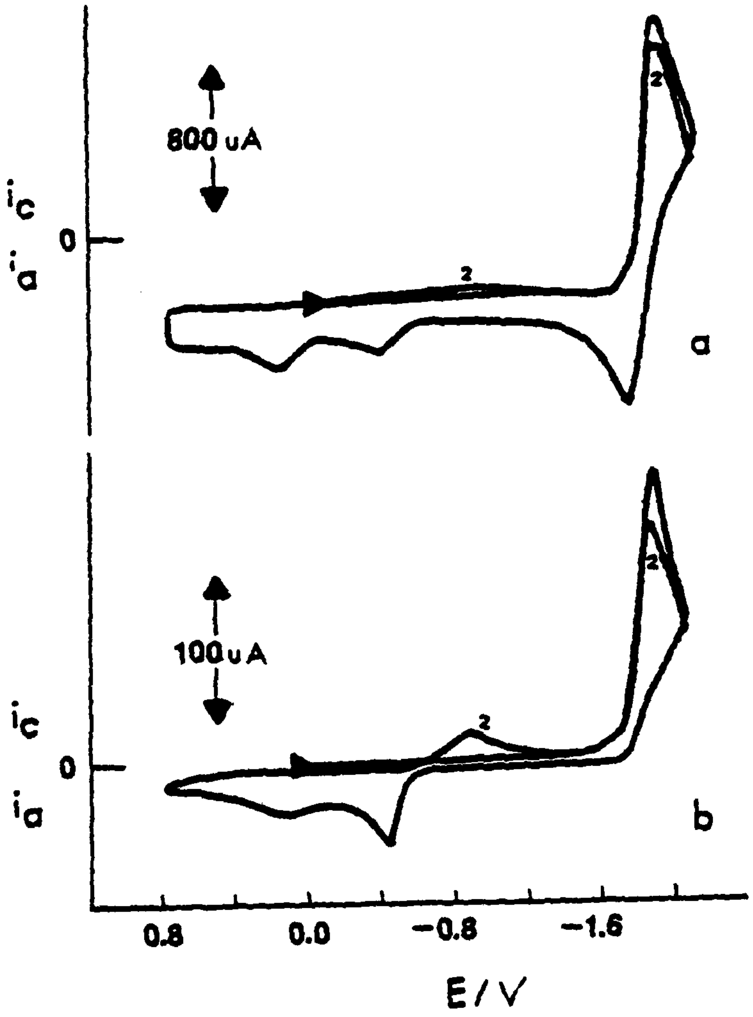
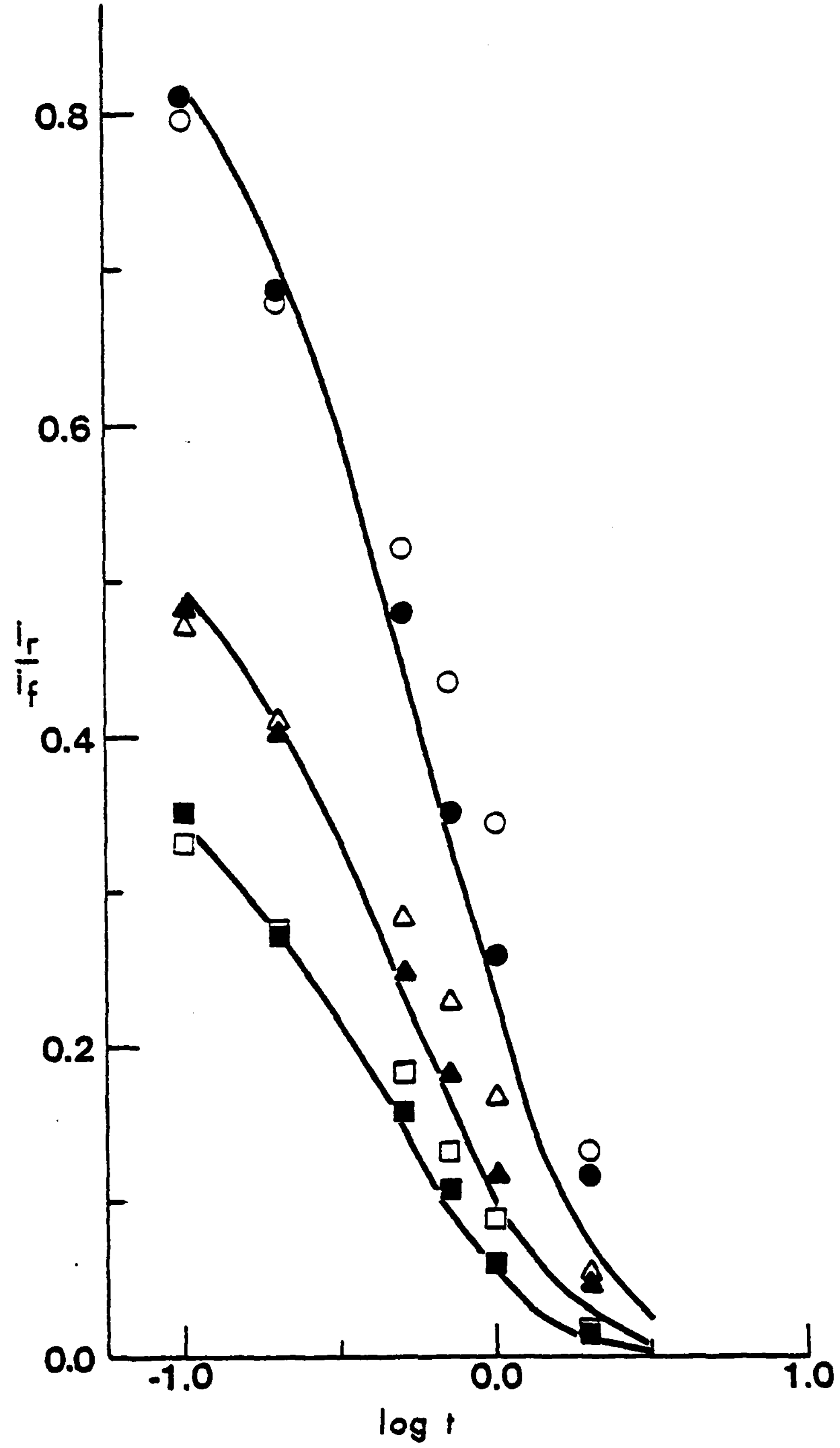

800 uA
i_c
0
i_a
2
2
a
100 uA
i_c
0
i_a
2
2
b
0.8
0.0
−0.8
−1.6
E / V

FIGURE IV-4

Double potential step chronoamperometry data for the reduction of $FlHNH_2$ in DMF-0.1 F $(n\text{-Bu})_4ClO_4$ at a planar platinum electrode at $-22^{\circ}C$. Concentrations are 2.46 mM (closed symbols) and 8.70 mM (open symbols). For the circles $(t-\tau_f)/\tau_f$ is 0.3; for the triangles 0.5; and for the squares 0.7. Theoretical curves are for $k = 0.8\ s^{-1}$. The applied potential for $t = 0$, $t \leq \tau$ and $t > \tau$ is -1.2 V, -2.1 V and -1.2 V, respectively.


0.8
0.6
0.4
0.2
0.0
$\frac{i_r}{i_f}$
-1.0
0.0
1.0
log t

constant for the reaction described by eq. IV-15 has not been reported but should be approximately one; pK values of 22.9 and 23.0 have been reported for FlH_2 and $FlHN(CH_3)_2$, respectively, in DMSO.[6]

N,N-Dimethyl-9-aminofluorene

Although $FlHNMe_2^{\cdot -}$ (k = 1.1 s^{-1} at $\underline{T}$= $-51^{\circ}C$, see Figure IV-5) is slightly less stable than $FlHNH_2^{\cdot -}$, analogous pathways for $FlHNMe_2$ and $FlHNH_2$ reductions may be written. The principal differences in the cyclic voltammetric behavior of these compounds occur when the corresponding conjugate bases of $FlNMe_2^-$ and $FlNH_2^-$ are oxidized. Whereas oxidation of $FlNH_2^-$ to give Fl=NH involves the relatively slow loss of a proton from $FlNH_2^{\cdot}$ to $FlNH_2^-$ and other indirectly electrogenerated bases, the absence of a rapid follow-up chemical reaction involving $FlNMe_2^{\cdot}$ causes $FlNMe_2^-$ ($\underline{E}_{p,c}$ = -0.16 V) to be oxidized with considerably greater difficulty than $FlNH_2^-$ ($\underline{E}_{p,a}$ =-0.52 V). If FlH^- has not been permitted sufficient time to react completely by abstracting a proton from $FlHNMe_2$, then the anodic processes which occur on the reverse, positive-going half cycle appear to resemble that of $FlNH_2^-$, *viz.*, $FlNMe_2^-$ and FlH^- afford single irreversible peaks at -0.16 and 0.16 V, repectively (Figure IV-6). However, if reaction of FlH^- with $FlHNMe_2$ is complete on the cyclic voltammetric time scale, then oxidation of $FlNMe_2^-$ occurs stepwise and reasonably reversibly, affording first the neutral radical, $FlNMe_2^{\cdot}$, at -0.16 V and then the cation, $FlNMe_2^+$, at 0.34 V. The stepwise oxidation of $FlNMe_2^-$ is most readily seen when $FlNMe_2^-$ is prepared *in situ* by action of electrogenerated $PhN{=}NPh^{2-}$ on $FlHNMe_2$ (Figure IV-7). The cathodic waves which appear on the first negative-going half cycle arise from the reversible reduction of PhN=NPh to $PhN{=}NPh^{\cdot -}$ ($\underline{E}_{p,c}$ = -0.60 V) and the

FIGURE IV-5

Double potential step chronoamperometric data for the reduction of $FlHN(CH_3)_2$ in DMF-0.1 F ($\underline{n}$-Bu)$_4$ClO$_4$ at a planar platinum electrode at $-51^{\circ}C$. Concentrations are 1.67 mM (closed symbols) and 6.71 mM (open symbols). For the circles $(t-\tau_f)/\tau_f$ is 0.3; for the triangles 0.5; and for the squares 0.7. Theoretical curves are for $k = 1.1\ s^{-1}$. The applied potential for $t = 0$, $t \leq \tau$ and $t > \tau$ is -1.2 V, -2.2 V and -1.2 V, respectively.

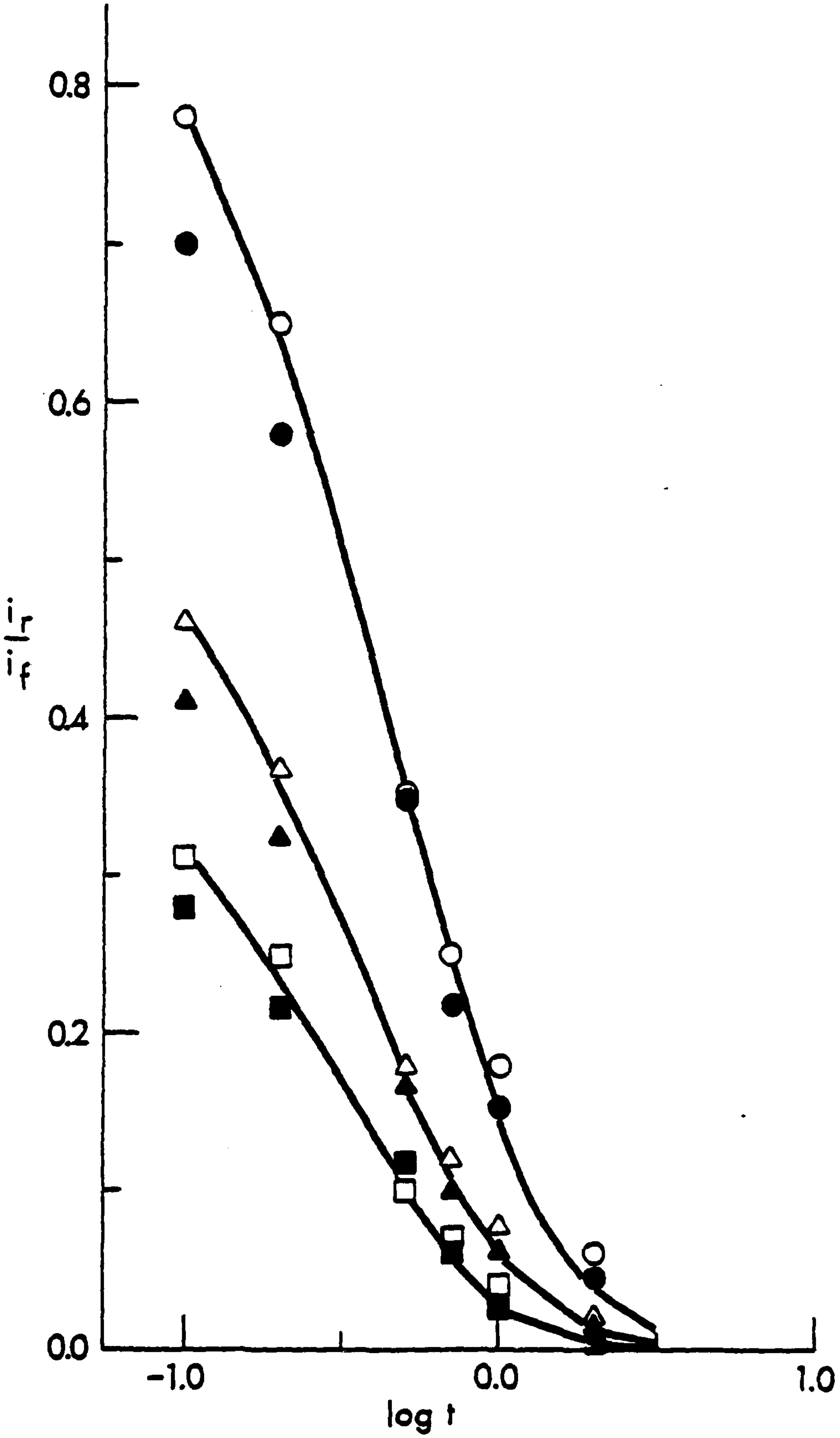
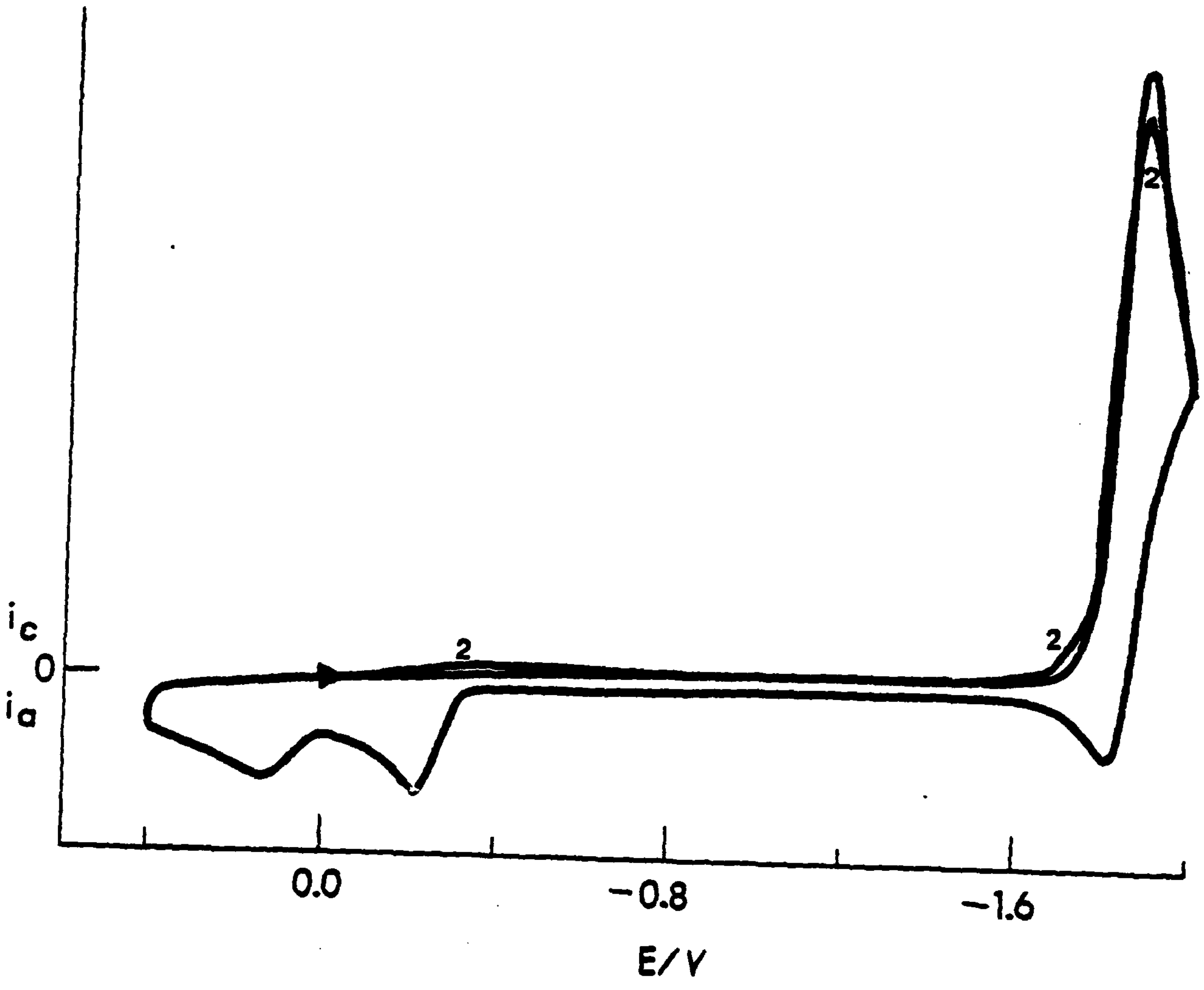

0.8
0.6
0.4
0.2
0.0
$\frac{i_r}{i_f}$
-1.0
0.0
1.0
log t

FIGURE IV-6

Cyclic voltammogram of 5.95 m$\underline{M}$ FlHN$(CH_3)_2$ in DMF-0.1 $\underline{F}$ ($\underline{n}$-Bu)$_4$ClO$_4$ at a planar platinum electrode. The scan was initiated in the negative-going direction at 0 V and a rate of 0.2 V/s. The small "2" indicates the second scan in the negative-going direction. The temperature was -51°C.



i_c
0
i_a
2
2
2
0.0
−0.8
−1.6
E/V

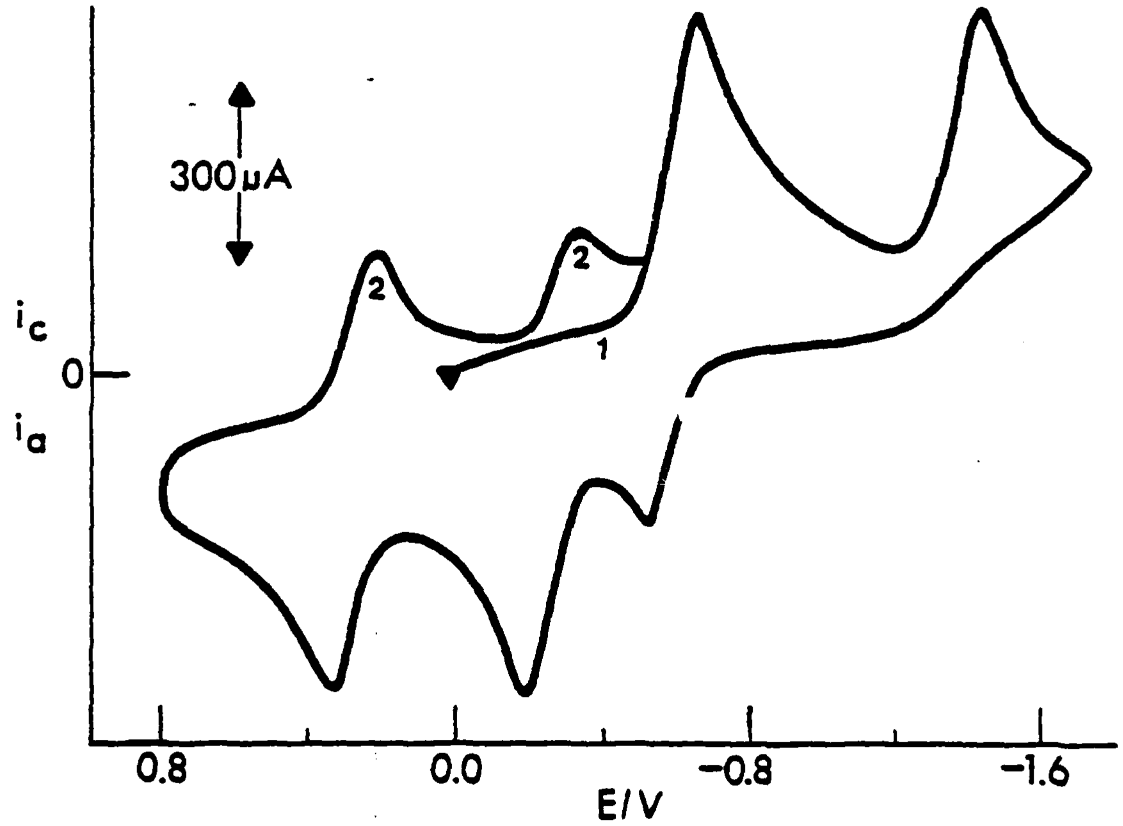
irreversible reduction of $\mathrm{PhN{=}NPh}^{\overline{\cdot}}$ to $\mathrm{PhN{=}NPH}^{2-}$ at -1.4 V. The latter species and/or $\mathrm{PhNH\bar{N}Ph}$ then rapidly abstract a proton from $\mathrm{FlHNMe_2}$ to give $\mathrm{FlNMe_2}^-$; successive one-electron oxidations of $\mathrm{FlNMe_2}^-$ account for the two reversible couples that appear at -0.16 and 0.34 V in Figure IV-7.

It should be noted that reduction of PhN=NPh gives substantially different results when $\mathrm{FlHNMe_2}$ is present than when $\mathrm{FlHNH_2}$ is present. Whereas $\mathrm{PhN{=}NPh}^{2-}$ proton abstracts from $\mathrm{FlHNMe_2}$ to give the expected products, PhNHNHPh and $\mathrm{FlNMe_2}^-$, reduction of PhN=NPh in the presence of $\mathrm{FlHNH_2}$ causes a chain reaction to ensue in which PhN=NPh is reduced to PhNHNHPh and $\mathrm{FlHNH_2}$ is oxidized to Fl=NH.[3] Two important steps in the propagation cycle are oxidation of $\mathrm{FlNH_2}^-$ by PhN=NPh and the reduction of $\mathrm{PhNH\dot{N}Ph}$ by $\mathrm{Fl{=}NH}^{\overline{\cdot}}$. A similar chain process occurs when PhN=NPh is reduced in the presence of 9-fluorenol, FlHOH.[3]

Finally, a comparison of Figures 6 and 7 will show that oxidation of $\mathrm{FlNMe_2}^-$ in the presence of FlH^- renders the $\mathrm{FlNMe_2}^-/\mathrm{FlNMe_2}^{\cdot}$ couple at -0.16 V irreversible and eliminates the anodic wave at 0.34 V which is attributed to the reversible oxidation of $\mathrm{FlNMe_2}^{\cdot}$ to $\mathrm{FlNMe_2}^{+}$. In addition, the oxidation of $\mathrm{FlNMe_2}^-$ in the presence of FlH^- affords a small, irreversible, cathodic peak on the second, negative-going half cycle at -1.72 V. Since (1) the reduction of bifluorenyl, $\mathrm{(FlH)_2}$, to its anion radical occurs irrevesibly with carbon-carbon bond cleavage near this potential,[2] (2) the oxidation of FlH^- occurs irreversibly to give both $\mathrm{(FlH)_2}$ and $\mathrm{FlH_2}$,[2] and (3) $\mathrm{FlNMe_2}^{\cdot}$ reacts rapidly in the presence of FlH^-, we suspect that $\mathrm{FlHFlNMe_2}$ may be formed by the coupling of $\mathrm{FlNMe_2}^{\cdot}$ with $\mathrm{FlH}^{\cdot}$. It is important to add that relatively rapid reaction of $\mathrm{FlNMe_2}^{\cdot}$ is observed even if the direct electrochemical

FIGURE IV-7

Cyclic voltammogram of 5.42 m$\underline{M}$ $FlHN(CH_3)_2$ and 1.21 m$\underline{M}$ azobenzene in DMF-0.1 $\underline{F}$ $(\underline{n}\text{-Bu})_4ClO_4$ at a planar platinum electrode. The scan was initiated at 0 V in the negative-going direction at a rate of 10 V/s. The temperature was 23°C.


300 µA
i_c
0
i_a
2
2
1
0.8
0.0
−0.8
−1.6
E/V

oxidation of FlH^- is not effected. Because the rapid carbon-carbon cleavage of $(\mathrm{FlH})_2^{\dot{-}}$ probably precludes the coupling of $\mathrm{FlNMe}_2^{\cdot}$ with FlH^- to give $\mathrm{FlHFlNME}_2^{\dot{-}}$, $\mathrm{FlH}^{\cdot}$ must be generated by an electrocatalytic pathway in which electrogenerated $\mathrm{FlNMe}_2^{\cdot}$ is the electron acceptor (eqs. IV-17 thru -19).

$$\mathrm{FlNMe}_2^- \longrightarrow \mathrm{FlNMe}_2^{\cdot} + e^- \qquad \text{(IV-17)}$$

$$\mathrm{FlNMe}_2^{\cdot} + \mathrm{FlH}^- \longrightarrow \mathrm{FlNMe}_2^- + \mathrm{FlH}^{\cdot} \qquad \text{(IV-18)}$$

$$\mathrm{FlH}^{\cdot} + \mathrm{FlNMe}_2^{\cdot} \longrightarrow \mathrm{FlHFlNMe}_2 \qquad \text{(IV-19)}$$

We have attempted to prove the feasibility of reactions IV-17 thru IV-19 by electrochemically oxidizing FlNMe_2^- in the presence of FlH^-. Unfortunately, either the _t_-BuO^- which is used in excess to prepare FlNMe_2^- and FlH^- and/or the FlH^- itself must abstract a proton from the coupling product, $\mathrm{FlHFlNMe}_2$, to give $\mathrm{Fl(NMe}_2\mathrm{)Fl}^-$. The latter species is oxidized irreversibly near 0 V to give unidentified products. The anodic wave which is due to the oxidation of $\mathrm{Fl(NMe}_2\mathrm{)Fl}^-$ can be seen in the cyclic voltammograms of FlHNMe_2 at certain combinations of temperature and scan rate as a shoulder on the FlH^- anodic peak.

Comparison of these results with those of previous workers. The electrochemical reduction of several N-substituted fluorenone and benzophenone imines has been reported to involve two steps of unequal magnitude in solvent systems where proton availability is low and a single two-electron step in protic media.[6,7] Although the corresponding amine is the assumed imine reduction product in protic media, dimeric products have been postulated in the reduction of certain sterically unhindered imines in aprotic media..[7,8] No evidence was obtained in this study for dimer formation upon reduction of either Fl=NH or $\mathrm{Ph_2C{=}NH}$. A small amount of fluorene was obtained when Fl=NH was reduced in the presence of diethyl malonate, but this is presumed to be the result of inadvertent reduction of the more-difficultly-reduced amine product, $FlHNH_2$.

Since neither the oxidation of $FlNH_2^-$ and $FlNMe_2^-$ nor the reduction of $FlHNH_2$ and $FlHNMe_2$ has been reported previously, we can only compare the redox behaviors of these compounds to those of the corresponding 9-hydroxy- and 9-methoxyfluorenes.[1] While parallels exist, for example, $FlOH^-$ and $FlNHPh^-$ are oxidized catalytically by electrogenerated Fl=O and Fl=NPh, respectively, significant differences are also seen, for example, electrocatalysis is only observed in the $FlNHPh^-$ system when a strong base is also present and no electrocatalysis could be detected for the $FlNH_2^-$ system under any solution conditions. The decomposition pathways for the anion radicals present another interesting contrast. Whereas hydroxide and alkoxide which are formed in the reductive cleavage of the carbon-oxygen bond of FlHOH and $FlHOCH_3$, respectively, are unreactive with respect to the C_9 proton, amide formed by the reductive cleavage of the carbon-nitrogen bond in $FlHNH_2$ reacts only by abstracting the C_9 proton from unreacted starting material. The selectivity of amide is unexpected, since the pK_a's of FlH_2, H_2O, and NH_3 in dipolar, aprotic solvents are approximately 22,[8] 31,[9] and 34,[10] respectively.

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VITA

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